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Phase Transformations and Ion Exchange During Early Age Carbonation

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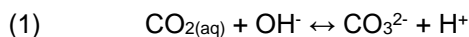
ABSTRACT

The exchange of ions during the dissolution of Portlandite and precipitation of newly formed carbonate phases, at the beginning of the carbonation reaction has been investigated. Changes in the isotopic composition of carbonates was determined using Time-of-Flight-Secondary Ion Mass Spectrometry and Raman spectroscopy. Samples of pure $\text{Ca}(^{18}\text{OH})_2$ were carbonated in humid air (containing almost exclusively ^{16}O) and characterized using Scanning Electron Microscopy and Raman Spectroscopy, aided by Density Functional Theory calculations. Results show that the carbonation process at high pH (i.e. >12) is a two-stage mechanism. The first stage occurs over a short period of time after the $\text{Ca}(^{18}\text{OH})_2$ is exposed to air and involves the dissolution of surface Ca^{2+} ions and hydroxyl $^{18}\text{OH}^-$ groups. The latter react directly with the dissolved CO_2 , leading to the formation of $\text{C}^{18}\text{O}^{16}\text{O}_2^{2-}$ ions containing 1/3 of ^{18}O . Since this ion is the precursor of the newly formed carbonate phases, a similar oxygen content was found in the precipitates. The $^{18}\text{O}:^{16}\text{O}$ ratio of 1:2 in the carbonates at the beginning of the reaction is in agreement with a carbonation model proposed by L  tolle and colleagues in 1990 [1] describing a direct reaction of CO_2 with the OH^- groups produced by the dissociation of water. The second stage of the reaction occurs within 24 hours of exposure to air and involves a rebalance of the oxygen isotopic composition in the carbonate phases with a higher concentration of ^{16}O .

1. INTRODUCTION

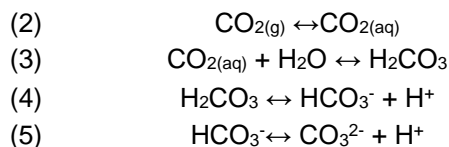
Carbonation of calcium hydroxide ($\text{Ca}(\text{OH})_2$) is an important process in many construction materials. However, the reactions of carbon dioxide (CO_2) and other ions such as the hydroxyl (OH^-) ion during the carbonation reaction is not yet fully understood.

In the 1990 Letolle and colleagues [1,2,3] suggested that at pH above 9, the direct reaction of CO_2 with the OH^- produced by the dissociation of water is the primary pathway for the formation of the carbonate ion (CO_3^{2-} ; equation 1).



Because of the reduced number of reactions involved, this pathway is supposed to be faster

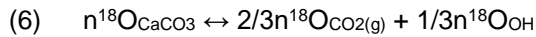
than the one leading to the formation of CO_3^{2-} from the reaction of CO_2 in natural waters at neutral pH as described in equations 2-5 [4].



Due to faster kinetics, the reaction path described in equation 1 prevents isotope equilibration of gaseous $\text{CO}_{2(\text{g})}$ with the dissolved $\text{CO}_{2(\text{aq})}$ [1,2,3]. In fact, since heavier isotopes react slower than lighter isotopes, in the carbonate precipitates at high pH it is expected a lower concentration of stable isotopes such as ^{18}O and ^{13}C compared to the carbonates

precipitated under equilibrium conditions. Examples of carbonate phases with differing isotopic signatures are limestone of marine and continental origins, and carbonates produced during cement setting [1,2,3].

Equilibrium in eq. 1 implies that the CO_3^{2-} ion contains a mixture of the isotopic composition of aqueous $\text{CO}_{2(\text{aq})}$ (similar to the isotopic composition of gaseous $\text{CO}_{2(\text{g})}$) and OH^- ions [1,2,3]. The ^{18}O composition of these carbonates ($n^{18}\text{O}$) can therefore be described by considering the abundance of ^{18}O in the different species, according to eq 6 where n is the number of ^{18}O atom.



In the 1990s Letolle and colleagues [1] calculated that one-third of the oxygen in the carbonates formed under high pH conditions is provided by the OH^- ions originated from the dissociation of H_2O molecules catalysing the reaction between $\text{Ca}(\text{OH})_2$ and aqueous $\text{CO}_{2(\text{aq})}$. This implies that the ^{18}O content of OH^- groups is related to the isotopic composition of H_2O . Letolle and colleagues didn't however provide any information on the role of OH^- ions produced by the dissolution of $\text{Ca}(\text{OH})_2$ on the isotopic composition of carbonate phases when this process takes place in lime.

2. EXPERIMENTAL PROCEDURE

To investigate the role of OH^- ions formed from the dissolution of $\text{Ca}(\text{OH})_2$ prior to the carbonation of lime, Portlandite containing exclusively ^{18}O ($\text{Ca}^{(18)\text{OH}}_2$) was synthesised through the direct hydration of calcium metal. Therefore, during carbonation the sample itself is by far the most significant source of ^{18}O (only a very limited contribution can be due to the CO_2 and H_2O), whereas the atmospheric H_2O and CO_2 are the only source of ^{16}O . Any isotopic mixture in the resulting carbonate phases can therefore provide knowledge of the most likely source of oxygen in the formation of carbonate ions and therefore information on the carbonation mechanism. This methodology is possible because the natural variation of stable isotopes, such as oxygen-18 (^{18}O), can be investigated using analytical techniques such as mass spectrometry and Raman spectroscopy. To investigate isotopic composition of carbonation reaction products, Time-of-Flight Secondary Ion Mass Spectrometry (ToF-SIMS) was employed. Specimens of $\text{Ca}^{(18)\text{OH}}_2$ were carbonated in air for 3 min (at 27% RH), 1, 8, and 137 days (50% RH). Characterisation was then undertaken using Scanning Electron Microscopy (SEM) and Raman Spectroscopy. Density Functional Theory (DFT) calculations

were also employed to corroborate the Raman shifts that are usually associated with different degrees of isotopic substitution in $\text{Ca}(\text{OH})_2$ and CaCO_3 . Details of materials and preparation methods, analytical instruments, SIMS data processing and the computational techniques used have been previously reported by Pesce et. al. (2017) [5]

3. RESULTS

SEM analysis of the $\text{Ca}^{(18)\text{OH}}_2$ specimen showed that this consisted of hexagonal plate-shaped crystals of diameter 200–400nm and crystalline particles of diameter 70–150nm. The presence of many irregular-shaped crystals is consistent with the exothermic reaction of Ca metal with water that caused rapid evaporation of the excess H_2^{18}O which, in turn is consistent with a high nucleation rate.

Raman spectra of the raw materials used in this experiment show that the peaks of the $\text{Ca}^{(18)\text{OH}}_2$ sample are shifted to lower wavenumbers compared to $\text{Ca}^{(16)\text{OH}}_2$. In particular, the peak at 356cm^{-1} is shifted to 337cm^{-1} , and the peak at 251cm^{-1} is shifted to 239cm^{-1} . It was also observed that the peak at 1086cm^{-1} resulting from limited carbonation of the specimens is shifted to 1067cm^{-1} .

Raman active modes of a natural $\text{Ca}^{(16)\text{OH}}_2$ and synthetic $\text{Ca}^{(18)\text{OH}}_2$, determined experimentally and also using DFT calculations, are presented in Tables 1 and 2 respectively. The systematic displacement of the predicted peaks relative to the experimental positions can be attributed to the estimation of bond length used in the DFT calculations.

Table 1. Experimental Raman active modes of $\text{Ca}^{(16)\text{OH}}_2$ and $\text{Ca}^{(18)\text{OH}}_2$

$\text{Ca}^{(16)\text{OH}}_2$	$\text{Ca}^{(18)\text{OH}}_2$	Δ
251	239	-12
356	337	-19
675	675	0

Table 2. Simulated Raman active modes of $\text{Ca}^{(16)\text{OH}}_2$ and $\text{Ca}^{(18)\text{OH}}_2$

$\text{Ca}^{(16)\text{OH}}_2$	$\text{Ca}^{(18)\text{OH}}_2$	Δ	Theoretical difference
256	242	-14	-14
381	361	-20	-19
715	715	0	0

Following carbonation of the two Portlandite specimens studied (containing ^{18}O and ^{16}O), the measured Raman peak positions of CaCO_3 are presented in Table 3. Table 4 shows the simulated Raman active modes for Calcite with different isotopic compositions ($\text{CaC}^{16}\text{O}_{3-x}^{18}\text{O}_x$), where x , is the number of ^{18}O atoms per

carbonate ion ($0 < x < 3$). Raman shift moves to lower wavenumbers with increasing x . The peak at approximately 152cm^{-1} in the experimental Raman spectra for both the ^{16}O and ^{18}O -specimens was poorly defined compared to the other peaks. The advantage of modelling is that the vibrational motion associated with each active mode can be identified. For example, the peak at 1086cm^{-1} is the symmetric stretch of the C–O bond in the carbonate ions, whereas the peak at 700cm^{-1} is an antisymmetric coupling between carbonate ions in different layers.

Table 3. Experimental Raman active modes of Calcite

Peak	$\text{CaCO}_3 \text{ } ^{18}\text{O} > ^{16}\text{O}$	$\text{CaCO}_3 \text{ } ^{18}\text{O} < ^{16}\text{O}$
1	152	152
2	277	282
3	698	713
4	1066	1086

Table 4. Simulated Raman active modes of Calcite and difference shown in brackets

$\text{CaC}^{16}\text{O}_3$	$\text{CaC}^{18}\text{O}^{16}\text{O}_2$	$\text{CaC}^{18}\text{O}_2^{16}\text{O}$	$\text{CaC}^{18}\text{O}_3$
159-165	156-162 (-3)	154-160 (-5)	151-57 (-8)
293	288(-5)	285(-8)	282(-11)
680	672-665(-8/-15)	661-652(-19/-28)	645(-35)
1055	1036(-19)	1015(-40)	995(-60)

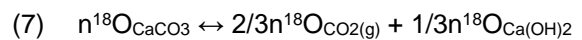
The ToF-SIMS allowed determination of the elemental, isotopic, or molecular composition of $\text{Ca}(\text{OH})_2$ surfaces to a maximum depth of 1–2 nm. Data for the carbonated $\text{Ca}(\text{OH})_2$ samples, showed a reduction in the relative intensities of species containing ^{18}O over time, and a simultaneous increase of the intensities of species containing ^{16}O . Species containing carbon showed an increase. This is clear evidence of the carbonation of Portlandite surfaces as secondary ions ejected from the surface destruction have greater carbon content. Table 5 reports the $^{18}\text{O}/^{16}\text{O}$ ratio calculated for all the secondary ions produced by the destruction of the surface over the duration of the experiment. Data shows an initial isotope ratio of 0.62 for positive ions and a ratio of 0.51 for negative ions. The weighted average value of 0.54 suggests that, at very early stages of carbonation, for every atom of ^{18}O in carbonate ions, there would be two ^{16}O (theoretical $^{18}\text{O}/^{16}\text{O}$ ratio $\frac{1}{2}$). However, from day 0 to day 1 the data shows a dramatic decrease in the $^{18}\text{O}/^{16}\text{O}$ ratio to a value of 0.038 that shows little variation in the following days. This value shows little variation after 137 days of carbonation. The isotopic ratio for positive and negative species converges toward the same value of 0.046, which is approximately double the value for natural samples [6].

Table 5. $^{18}\text{O}/^{16}\text{O}$ ratio calculated from the intensity of the SIMS counts for the ionic species with positive and negative polarity

	Day 0	Day 1	Day 8	Day 137
$[^{18}\text{O}/^{16}\text{O}]^+$	0.616	0.057	0.044	0.046
$[^{18}\text{O}/^{16}\text{O}]^-$	0.509	0.032	0.029	0.046
Weighted average	0.537	0.038	0.033	0.046

4. DISCUSSION

The combination of the results of the atomistic modelling of the materials with different isotopic composition with the ToF-SIMS experiments show that it is possible to elucidate the carbonation mechanism of hydrous materials. The shift observed for the Raman peaks of Portlandite and calcite containing ^{18}O , can be associated with the variations in the isotopic composition of the minerals and this hypothesis is supported by *ab initio* calculations with DFT. In the case of Portlandite, the shifts in Raman peaks arise from substitution of all the ^{16}O with ^{18}O , whereas in the carbonate phases formed after the reaction with atmospheric CO_2 the shifts are due to the partial substitution of ^{16}O with ^{18}O . DFT data confirm that the experimental peaks at 152, 271, 698, and 1066cm^{-1} are associated with calcite containing 1/3 of ^{18}O ($^{18}\text{O}/^{16}\text{O}$ ratio 0.5). The main vibrational fingerprint of this phase could be identified in the peak at 1066cm^{-1} . The peak at 1083cm^{-1} belongs to ^{16}O -calcite, which is a minor phase at the beginning of the reaction which then grows over the time. ToF-SIMS results show that at the early stage of carbonation (~ 3 min exposure to air), the ratio is 0.54. This value is in good agreement with the results of our theoretical analysis of Raman shifts and with Letolle's proposition [1,2,3]. This suggest that in the carbonate precipitates at high pH, 2/3 of oxygen is supplied by CO_2 , whereas 1/3 of the oxygen is provided by OH^- ions. However, unlike Letolle's proposition (suggesting that the OH^- groups involved in the carbonation originate from the dissociation of H_2O molecules), our results clearly demonstrate that the $\text{Ca}(\text{OH})_2$ plays an important role in the formation of OH^- groups. As a consequence, it is possible to infer that in highly alkaline conditions, the isotopic composition of precipitated carbonates, which is generally described by eq 6, can be rewritten by considering the abundance of ^{18}O in the CO_2 and in the $\text{Ca}(\text{OH})_2$ as reported in eq 7.



This new equation marks the very early stage of the carbonation reaction where the dissolution of the surface is the rate-limiting step. Although this equation is a simplification of the real process

(since it omits the equilibration of $^{18}\text{OH}^-$ ions from the Portlandite surface and water), it can be used to describe the process in basic terms.

Subsequent to the formation of ^{18}O -rich carbonate phases in the first stage of the carbonation mechanisms (when the dissolution of Portlandite surfaces must occur), our ToF-SIMS data show a dramatic reduction in $^{18}\text{O}/^{16}\text{O}$ ratio within the first day of carbonation. This is also shown by the growth of the Raman peak at 1083cm^{-1} of ^{16}O -calcite over time and can be explained by the transformation of the initial metastable carbonates into more stable phases over time. A possible explanation for re-equilibration of the $^{18}\text{O}/^{16}\text{O}$ ratio is the dissolution of metastable phases that give up some ^{18}O and the subsequent recrystallization of more stable phases that acquire ^{16}O when precipitated under equilibrium conditions.

This marks the second stage of carbonation, which involves the transformation of carbonate phases from lesser stable to more stable forms. The transformation mechanism of ACC to calcite can be described as a two stage process: (1) ACC particles rapidly dehydrate and crystallize forming individual particles of vaterite; (2) the vaterite dissolves and re-precipitates as calcite [7]. Stage 1 mainly entails the release of water molecules initially embedded in the structure of hydrated phases. Stage 2 involves the release of CO_3^{2-} ions that, according to eq.'s 2–5, can lead to an exchange of oxygen atoms with the water molecules. It is possible to infer that our data is consistent with this proposition. The oxygen exchange and the formation of new carbonate phases richer in ^{16}O at the surface of the carbonate phases initially formed (stage 1) explains the sudden variation of the $^{18}\text{O}/^{16}\text{O}$ ratio within the first 24h. Therefore, it is possible to deduce that, whereas precipitation of metastable phases takes place under non-equilibrium conditions (i.e., at high pH, which does not allow isotope equilibration), the dissolution and precipitation mechanism leading to the formation of stable carbonate phases and the precipitation of new carbonate phases richer in ^{16}O occurs at lower pH allowing an isotopic equilibrium of carbonates. It is worth noting that in our experiments this equilibration occurred within the initial 24h even at 50% RH (a relatively low RH value for carbonation), and this suggests that stage 2 of the carbonation is a fast kinetic pathway.

3. CONCLUSIONS

These results provide new insights into the mechanism of Portlandite carbonation. It has been demonstrated that during the early stage of carbonation reaction (first 3 min, in our

experiments) the surface OH^- groups of Portlandite are the main source of oxygen in the formation of CO_3^{2-} . Hence the growth of carbonate begins by the dissolution of OH^- and Ca^{2+} followed by the formation of metastable CaCO_3 . The second stage of the reaction occurs within 24h following the start of carbonation. This involves the transformation of the metastable carbonate phases into stable calcite. During this transformation water is released, which is the source of O for the formation of new CO_3^{2-} . The work demonstrates how artificial isotopic doping can be applied to study processes such as carbonation and have elucidated the early carbonation process.

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